

DETERMINATION OF PHONON DISPERSION CURVES AT GIGAPASCAL PRESSURES BY INELASTIC X-RAY SCATTERING

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The study of phonon dispersion curves of materials under hydrostatic pressure provides important information such as the evolution of sound velocities, elastic constants, interatomic potentials, phase transition mechanisms, etc. Until very recently, coherent inelastic neutron scattering was the only spectroscopic technique, which allowed performing these types of studies up to typically 10 GPa. Today, inelastic X-ray scattering with meV energy resolution provides a complementary spectroscopic technique, where, using diamond anvil cell techniques, pressures beyond 100 GPa can be reached.

Keywords: Inelastic X-ray scattering; Pressure; Phonon dispersion; Argon; Iron

INTRODUCTION

The knowledge of the structure and the dynamics of condensed matter on an atomic scale is of central importance in order to correctly explain macroscopic phenomena such as mechanical stability, materials strength, as well as thermodynamic and transport properties. While diffraction techniques with wavelengths in the Angstrom regime allow determining the structure of matter, inelastic scattering techniques probe the dynamics, *i.e.* the collective phonon or local vibrational modes. The experimentally observable parameter is the dynamical structure factor, $S(\mathbf{Q}, E)$, where \mathbf{Q} denotes the momentum- and E the energy transfer to the system. In the classical limit, $S(\mathbf{Q}, E)$ is the space- and time-Fourier transform of the density-density correlation function [1]. Therefore, the momentum transfer Q is directly related to a spatial distance or wavelength $2\pi/Q$, and the energy transfer E to a characteristic time h/E . Depending on the probing particle or radiation, different regions in the Q - E plane are occupied. While Brillouin light scattering techniques cover energy transfers typical for phonon

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energies, its maximum achievable momentum transfer of a few 10^{-2} nm^{-1} does not allow to map out full phonon dispersion curves. In contrast to this, energy and wavelength of thermal neutrons are well matched with typical phonon momenta and energies. Inelastic neutron scattering (INS) has therefore been the technique of choice to determine phonon dispersion curves and, more generally, the high-frequency dynamics of condensed matter.

In recent years, inelastic X-ray scattering (IXS) with very high energy resolution ($\Delta E/E = 10^{-7}$ or better) has become an attractive alternative [2]. This is especially true in the study of disordered systems, where well defined excitations are only existing up to momentum transfers of a few nm^{-1} . These cannot be studied by INS in systems with a large speed of sound (typically larger than 2000 m/s) due to kinematic limitations [3]. Amongst other complementarities, the most important difference between INS and IXS in the study of matter under high pressure is the size of the probing beam, which is intimately related to the maximum achievable pressure. Remarkable developments in neutron high-pressure techniques allow nowadays carrying out experiments on samples of several 10 mm^3 up to 10 GPa [4, 5]. However, the pressure regime above 10 GPa can currently not be exploited, since the requirement of a smaller sample volume would lead to an unacceptable reduction of the scattered signal. These limitations can be overcome by IXS with meV energy resolution, using diamond anvil cell (DAC) techniques. Thanks to the high collimation of X-rays generated by undulators on dedicated synchrotron radiation facilities and associated X-ray optics, beam sizes on the sample of a few tens of micrometers can be routinely obtained. Moreover, the photon-matter interaction is governed by photoelectric absorption, yielding an optimum sample thickness in the micrometer range for high Z materials. Therefore, typical sample thickness and lateral size are well compatible with the constraints of a DAC, and, thus, the reduction of the signal stays moderate.

In the following, the experimental setup and two different examples of IXS studies in a DAC will be presented in order to illustrate the possibilities that this new technique offers to high pressure science.

EXPERIMENTAL DETAILS

Two beamlines, ID16 and ID28, are dedicated to phonon dispersion studies at the European Synchrotron Radiation Facility. They are based on the following principles: The X-ray beam from the undulator source is monochromatized by a cryogenically cooled silicon (1 1 1) double crystal setup and a high-energy resolution silicon backscattering monochromator [3, 6]. The backscattered beam impinges on a gold-coated toroidal mirror which provides a focal spot at the sample position of $250 \mu\text{m}$ (horizontal) and $60 \mu\text{m}$ (vertical) size. The scattered photons are energy-analyzed by a Rowland circle five-crystal spectrometer [7, 8]. The energy-analyzed photons are detected by a Peltier-cooled silicon diode detector. The momentum transfer $Q = 2k_i \sin(\theta_s/2)$, where k_i is the incident photon wave vector and θ_s is the scattering angle, is selected by rotating the spectrometer around a vertical axis passing through the scattering sample in the horizontal plane. The energy scans are performed by varying the monochromator temperature while the analyzer temperature is kept fixed. Conversion from the temperature scale to the energy scale is accomplished by the following relation: $\Delta E/E = \alpha \Delta T$, where $\alpha = 2.58 \times 10^{-6}$ is the linear thermal expansion coefficient of silicon at room temperature.

PHONON ENERGIES IN ARGON SINGLE CRYSTAL AT 3.1 GPa [6]

Figure 1 shows a typical IXS scan, recorded at 20 nm^{-1} with a momentum transfer approximately along the (1 0 0) direction. The spectrum is characterised by a central line at $E = 0 \text{ meV}$ arising from elastic scattering, and two pairs of phonons, corresponding to

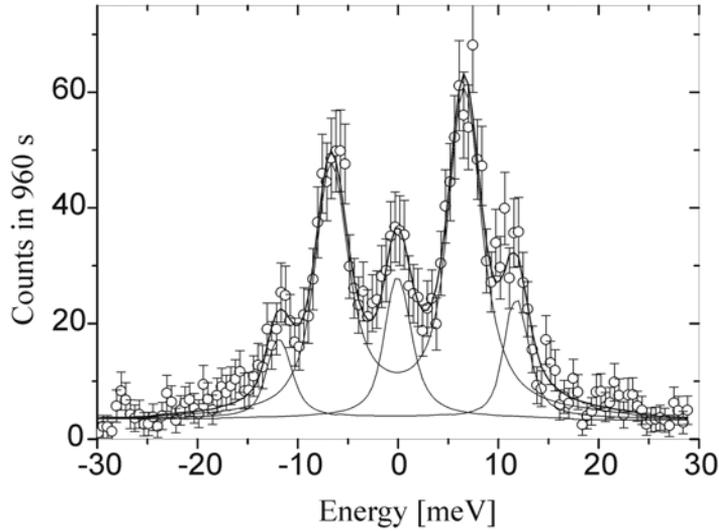


FIGURE 1 Typical IXS scan of Argon single crystal at $Q=20 \text{ nm}^{-1}$, $T=297 \text{ K}$ and $P=3.1 \text{ GPa}$. The experimental data (open circles) with their error bars are shown together with a fit, resulting from a set of five Lorentzians, convoluted with the experimental resolution function.

the energy-loss ($E > 0$) and energy-gain ($E < 0$) of the incident photon. These phonons are of longitudinal and transverse acoustic nature. Data were recorded at eight different momentum transfers and the resulting dispersion curve is shown in Figure 2. From a sine fit the longitudinal (c_{LA}) and transversal (c_{TA}) acoustic sound velocities are derived: $c_{\text{LA}} = 3250 \pm 50 \text{ m/s}$, $c_{\text{TA}} = 2000 \pm 50 \text{ m/s}$. They are in very good agreement with Brillouin

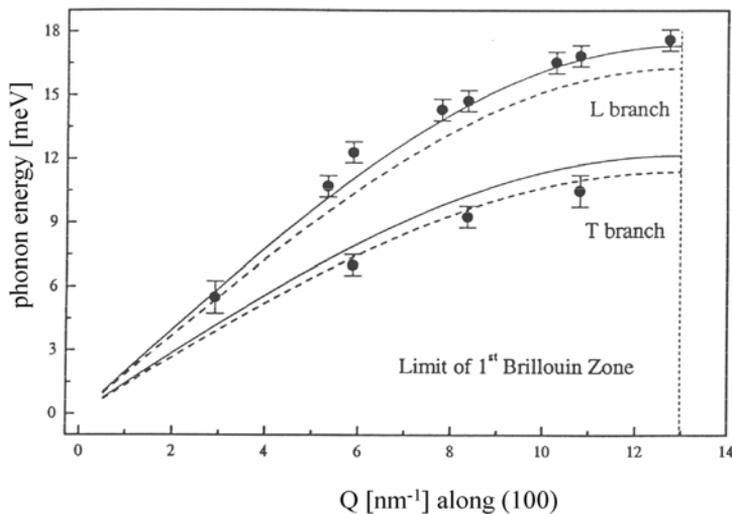


FIGURE 2 Phonon dispersion of Argon along the (100) direction. Full circles: IXS data, full line: calculations using the HFDID1 potential [10], dashed line: calculations using the exp-6 potential [11].

scattering data [9]. With the density ρ and the bulk modulus B , obtained from the experimental equation of state, the elastic constants C_{11} , C_{44} and C_{12} can be calculated ($C_{11} = \rho c_{LA}^2$, $C_{44} = \rho c_{TA}^2$, $C_{12} = (3B - C_{11})/2$). Furthermore, the Cauchy relation ($\delta = (C_{44} - C_{12} + 2P)/C_{12}$) yields a value of $\delta = 0.4$, in agreement with earlier results of a Brillouin scattering experiment [9]. The phonon dispersion has been calculated, using two different pair potentials: the state-of-the-art pair potential of Ar (HFDID1) which is constrained by a large set of pair potential properties [10], and a pair potential inverted from the Hugoniot measurements (exp-6) that includes many-body contributions averaged in its two-body form [11]. While both potentials represent well the equation of state within the error bars [12], none of them describes correctly both acoustic dispersion branches (see Fig. 2), thus showing that the dynamic properties are more influenced by many-body interactions than the static ones.

HCP-IRON FROM 19 TO 110 GPa [10]

The experimental determination of the elastic properties of hexagonal-closed-packed (hcp) iron up to very high pressures is of central importance for geophysics, since hcp-iron is believed to be the main component of the inner core of the Earth. In contrast to indirect experimental techniques such as X-ray diffraction lattice strain measurements [14, 15], nuclear inelastic scattering [16] and Raman scattering [17], IXS from a polycrystalline sample provides a direct determination of the (orientationally averaged) longitudinal sound velocity. The experiment was performed for pressures ranging from 19 to 110 GPa. Figure 3 reports the resulting sound velocity as a function of density – derived in the same manner as for the Argon experiment from five different $E(Q)$ -points. The IXS results agree very well in the region of overlap with Hugoniot measurements [18]. The sound velocity follows a Birch law (linear dependence between density and sound velocity). This law, extrapolated to higher pressure values (or higher specific mass), does not agree with Reference Earth Model seismic data [19], thus suggesting a 4 to 5% lighter inner core than hcp-iron. This discrepancy could be explained either by the presence of light elements in the inner core or by another iron phase stable at the pressure and temperature conditions of the Earth's inner core.

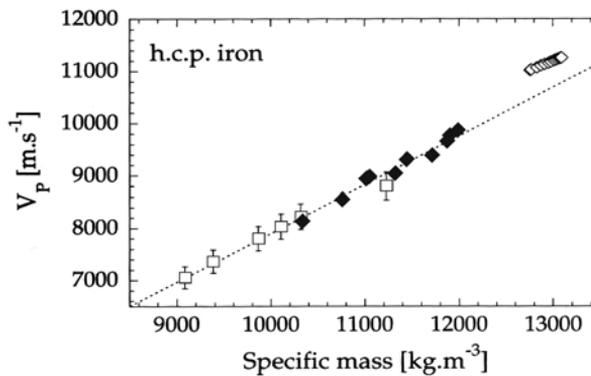


FIGURE 3 Longitudinal acoustic wave velocity of hcp iron [13]. Open squares: IXS data, solid diamonds: shock wave measurements [18], open diamonds: Reference Earth Model seismic data [19].

CONCLUSIONS

IXS with meV energy resolution promises to be a very valuable tool in the study of matter under extreme pressure for a large variety of materials ranging from low Z liquids to high Z single- and polycrystalline systems.

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